MISSOURI DEPARTMENT OF NATURAL RESOURCES
AIR AND LAND PROTECTION DIVISION
ENVIRONMENTAL SERVICES PROGRAM
Standard Operating Procedures

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SOP TITLE: Sample Collection and Field Analysis for Dissolved Oxygen Using a Membrane Electrode Meter

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SUMMARY OF REVISIONS: Not applicable. This is a new SOP.

APPLICABILITY: The procedures outlined in this SOP apply to all ESP personnel who measure dissolved oxygen in the field.

DISTRIBUTION: MoDNR Intranet
ESP, SOP Coordinator
ESP, WQMS, Section Chief
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RECERTIFICATION RECORD:

Date Reviewed				
Initials				

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure provides the Environmental Services Program (ESP) field personnel with guidance on the operation and maintenance of the various dissolved oxygen (D.O.) meters and on the analysis of D.O. during their field investigations.

2.0 PERSONNEL QUALIFICATIONS

Field personnel shall have a working knowledge of field sample collection procedures and will have at a minimum either attended the department-sponsored Inspection and Enforcement training or received training from an MDNR employee knowledgeable on proper sample collection procedures.

3.0 HEALTH AND SAFETY

Field activities involving the collection of D.O. measurements may include working in and/or around a type of waste stream. Field personnel shall protect themselves by wearing the appropriate level of personal protection equipment.

4.0 SAMPLING CONSIDERATIONS

4.1 A D.O. sample has no holding time and should be analyzed immediately upon collection. To obtain accurate measurements, D.O. analysis should be performed on-site and in situ.

4.2 When collecting D.O. measurements, it is important that the field personnel record observations to include: the time of day, weather conditions, water temperature, unusual stream/lake characteristics (e.g., septic conditions, algae growth, etc.), the stream segment from where the field measurement was collected (e.g., riffle, pool or run) or the lake depth from where the D.O. was collected.

4.3 D.O. measurements should not be collected from areas with turbulent flow, still water or from the stream bank, unless these conditions are representative of the stream reach or are required by the study objectives.

4.4 Normally, the D.O. probe is placed directly into the body of water, lake, stream, etc., that is being measured. However, due to high flow conditions, access, etc., it may be necessary to collect a sample in a bucket or other container. When this is necessary, care must be taken not to aerate the sample upon collection. D.O. measurements must be made immediately after the sample has been collected.

5.0 GENERAL OVERVIEW

5.1 The ability of a body of water to support aquatic life is dependent on the level of D.O. contained within it. The Missouri Water Quality Standards specify that the minimum concentration of D.O. to support aquatic life is 5.0 mg/L for cool and warm waters (6.0 mg/L for cold waters). Accurate D.O. levels can be determined with relative ease through

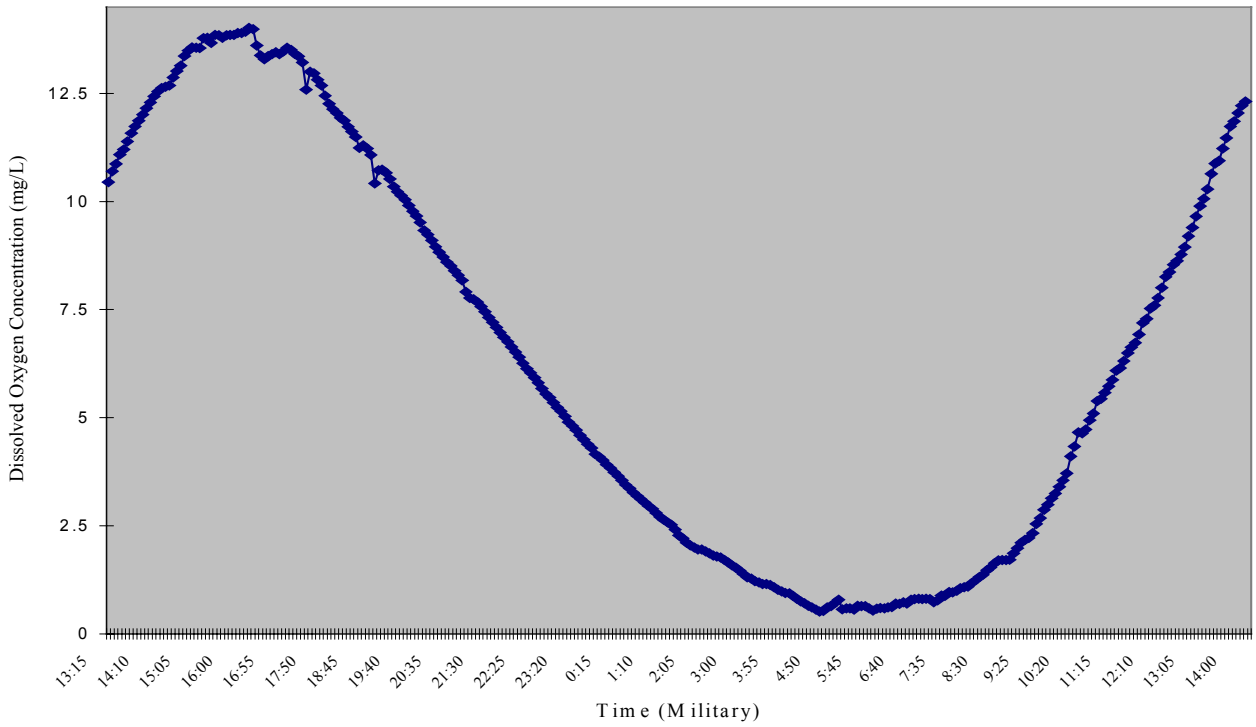
the use of a membrane electrode meter.

5.2 The level of D.O. in natural water systems (e.g. streams and lakes) and wastewater depends on the physical, chemical, and biochemical activities in the body of water. One or more of these factors can influence the dissolved oxygen concentrations of a water system (refer to sections 5.2.1 – 5.2.3 for examples).

5.2.1 Oxygen becomes dissolved in water by a number of means. A water system may receive oxygen through diffusion from the atmosphere, aeration (as water tumbles through a riffle area or over a fall), and photosynthesis.

5.2.2 Non-point source runoff or discharges containing phosphorous and nitrogen compounds can significantly alter oxygen levels in water systems. These compounds are readily taken up by aquatic plants, stimulating growth and reproduction, which may result in algal blooms. As a by-product of the photosynthetic process, plants produce oxygen, initially elevating the D.O. concentration. In turn, as the plants respire, and as they die and decompose, they consume oxygen. Therefore, over a 24-hour period, the oxygen levels will generally rise through photosynthetic activity during daylight hours and then drop during the evening hours as the respiration and bacterial breakdown process occurs. Through this daily cycle, a dissolved oxygen curve can be plotted. In the presence of an algal bloom, the graph below is an example of what the dissolved oxygen curve may look like over a 24-hour period.

An example of a dissolved oxygen curve over a 24-hour period.



5.2.3 Water temperature affects the amount of dissolved oxygen that a water system can hold. Cooler water can typically hold more oxygen, while warmer water can hold less.

6.0 DISSOLVED OXYGEN METERS

6.1 There are four Yellow Springs Instrument Company (YSI) D.O. meters commonly used by the Environmental Services Program field personnel. The operation, handling, and storage of the YSI D.O. meter Models 54 and 57 (analog), and Models 58 and 550 (digital) will be discussed.

6.2 The D.O. meters use the polargraphic (Clark-type) membrane probe with built-in thermistors for temperature measurement and compensation. The thin, permeable membrane stretched over the probe isolates the sensor elements from the environment, but allows oxygen and certain other gases to enter. When a polarizing voltage is applied across the sensor, oxygen that has passed through the membrane reacts with the cathode, causing a current to flow. The D.O. is then expressed as mg/L or percent saturation (see YSI Dissolved Oxygen Meter Operations Manual).

Note: D.O. readings recorded on the chain-of-custody record should be expressed as mg/L.

6.3 For accurate D.O. readings, water movement of one foot per second or more is required across the D.O. probe membrane. This is so the oxygen-depleted layer of the sample at the membrane surface is flushed away and replenished. A moving stream can provide this motion; alternatively, the probe can be gently moved through the sample by hand (refer to the YSI Dissolved Oxygen Meter Operations Manual).

7.0 METER AND PROBE CHECKOUT PROCEDURES

7.1 YSI Dissolved Oxygen Meter Models 54 and 57 (analog meters)

7.1.1 The meter should be placed in the intended position (vertical, tilted or horizontal) prior to calibration and field use. Readjustment may be necessary when the instrument's operating position is changed.

7.1.2 Adjust the SALINITY control knob to the zero position.

7.1.3 Check the meter's mechanical zero. The needle should read zero mg/L when the meter is in the OFF position. If the meter does not read zero, adjust the needle by turning the screw located just below the meter face until it aligns with the zero.

7.1.4 Turn the selector knob to RED LINE and adjust the RED LINE knob until the needle aligns with the RED LINE located on the meter's face (at the 31°C position).

Note: The RED LINE adjustment is a battery check of the instrument. If the meter cannot be set on RED LINE or the needle drifts after setting, the batteries must be replaced (refer to the YSI Dissolved Oxygen Meter Instruction Manual).

7.1.5 Switch the selector knob to ZERO and adjust the needle with the zero control knob until the meter needle aligns to read zero mg/L.

7.1.6 Check the meter's probe and membrane. The membrane should appear clear and have no cracks. Check to make sure there are no air bubbles under the membrane and that the sensor is shiny gold in color. If any of these conditions do not exist, the probe must be reconditioned prior to use (refer to the YSI Dissolved Oxygen Meter Instruction Manual).

7.1.7 Prepare the D.O. probe by exposing the probe to moist air by placing it into the small calibration bottle along with a water-moistened sponge. The probe can also be wrapped loosely with a damp cloth taking care not to touch the membrane. If wrapped in a damp cloth, the probe should be placed in a closed environment (e.g. plastic bag or container) to prevent evaporation (resulting in cooler air temperatures) from occurring.

7.1.8 Before calibrating (see section 8.0), allow the meter to warm up and the probe to polarize 20–30 minutes for optimum probe stabilization. Whenever the meter has been off or the probe has been disconnected, the probe must be allowed to repolarize and the meter must be recalibrated.

7.1.9 Calibrate the meter (see section 8.0)

7.2 YSI Dissolved Oxygen Meter Model 58 (digital display)

7.2.1 The YSI Model 58 may be used in a vertical, horizontal or tilted position. It may be carried or moved during use without affecting its accuracy or stability of measurement.

7.2.2 Check the meter's probe and membrane as described in section 7.1.6.

7.2.3 Prepare the probe as described in section 7.1.7.

7.2.4 Zero the instrument. Set the function switch to ZERO and adjust the display to read 0.00 with the 0_2 Zero control knob.

7.2.5 As stated in section 7.1.9, allow the meter to warm up and the probe to polarize 20-30 minutes for optimum probe stabilization before calibrating (see section 8.0). Again, whenever the meter has been off or the probe has been disconnected, the probe must be allowed to repolaraize and the meter must be recalibrated before use.

7.2.6 Calibrate the meter (see section 8.0).

7.3 YSI Handheld Dissolved Oxygen Meter Model 550 (digital display)

7.3.1 The YSI Model 550 may be used in a vertical, horizontal or tilted position. It may be carried or moved during use without affecting its accuracy or stability of measurement.

7.3.2 Check the meter's probe and membrane as described in section 7.1.6.

7.3.3 A built in calibration chamber is incorporated in the YSI Model 550 dissolved oxygen meter case. Prior to calibration, ensure the sponge located inside the calibration chamber is moist, and then re-insert the probe.

7.3.4 Turn the meter on by pressing the ON/OFF button and allow the probe to polarize before calibrating (usually 20-30 minutes). Again, whenever the meter has been off or the probe has been disconnected, the probe must be allowed to repolarize and the meter must be recalibrated before use.

7.3.5 Calibrate the meter (see section 8.0).

8.0 DISSOLVED OXYGEN CALIBRATION PROCEDURES

8.1 Daily calibration is generally appropriate, however, the calibration can be disturbed by physical shock, touching the membrane, fouling of the membrane or drying out of the electrolyte. The calibration should be periodically checked after conducting a series of measurements (refer to Section 11.1 for additional information).

8.2 The operator has a choice of three calibration methods: Winkler titration, air-saturated water, and air. Experience has shown that air calibration is quite reliable, and far simpler than the other two methods when field calibrating. The Winkler titration method is excellent for calibrating in a laboratory environment. Of the three calibration methods, the air-saturated water method is a less precise method because it is difficult to obtain precise and stable saturation. The following sections will discuss calibration by air and the Winkler titration method.

8.3 As discussed in section 8.2, air calibration is accurate, and is the quickest and the simplest field calibration procedure. However, the calibration value has to be corrected to either the local altitude above mean sea level or the "true" barometric pressure. The altitude adjustment is an acceptable calibration correction method. The altitudes across the state of Missouri vary from 265 ft. to 1,316 ft. Correction values for these altitudes range from 99% to 96%, respectively. For consistency, field personnel shall calibrate all the meters using a 700 ft. correction value (97%). With this in mind, there may be slight differences (approximately 1% - 2% error) in D.O. readings collected from areas of Missouri located above or below 700 ft. This corresponds to approximately a 0.3 mg/L difference in D.O. ranges normally encountered in the field.

8.4 Calibration by air using the YSI Dissolved Oxygen Meter Models 54, 57 and 58

8.4.1 Prepare the meter(s) as described in section 7.1 (Models 54 and 57) and 7.2 (Model 58).

8.4.2 With the probe placed into the calibration bottle, switch the selection knob to TEMP and read the air temperature. Refer to the solubility of oxygen chart located on the back panel of the meter (referred to on the meter as Table I) or Table I of Appendix A. Select the correct calibration value in mg/L by referencing the air temperature reading with solubility of oxygen chart.

8.4.3 Generally, you would determine the local altitude using a topographic map. Then reference the pressure/altitude chart located on the back panel of the meter (referred to on the meter as Table II) or Table II of Appendix A to determine the calibration correction factor. However, as stated in section 8.3, ESP field personnel shall use 700 ft. as the altitude correction value when calibrating the D.O. meters.

Example:

- Probe air temperature = 21 °C, Altitude = 700 ft.
- From Table I (located on the back panel of the meter) the calibration value for 21 °C is 8.92 mg/L.
- From Table II (located on the back panel of the meter) the altitude factor for 700 ft. is 97%. Multiply the calibration value by the correction factor.
- The correct calibration value is 8.65 mg/L.

8.4.4 Turn the selection knob to the appropriate mg/L range, using the 0_2 CALIB or CAL knob, and adjust until the meter reads the correct calibration value. When using the analog meter, select the appropriate mg/L range (0 to 5, 0 to 10 or 0 to 20 mg/L). Select the scale with the lowest range in which the value is contained.

8.4.5 The meter is now air calibrated and is ready to collect measurements.

8.5 Calibration by air using the YSI Dissolved Oxygen Meter Model 550

8.5.1 With the probe in the calibration chamber, switch the meter to the percent saturation mode (%) by pressing the MODE key.

8.5.2 To enter the calibration menu, press both the UP ARROW and DOWN ARROW keys at the same time. CAL will be displayed in the lower left of the display.

8.5.3 The meter will prompt you to enter the local altitude in hundreds of feet. Use the UP or DOWN arrow keys to increase or decrease the altitude to 700 ft, then press the ENTER key. The calibration value will be displayed in the lower right corner, CAL in the lower left corner and the current D.O. reading (before calibration) on the main display.

8.5.4 Wait for the D.O. reading to stabilize, then press the ENTER key. The meter will prompt you to enter the approximate salinity of the water that you are about to

analyze. For freshwater systems, a value of zero parts per thousand (PPT) should be scrolled in using the UP or DOWN ARROW key.

8.5.5 Once the appropriate salinity value has been selected, press the ENTER key. The meter will then automatically advance to measurement mode. The meter is air calibrated and ready to collect measurements in the percent saturation mode.

8.5.6 Switch the meter to read in mg/L by pressing the MODE key.

8.6 Calibration by the Winkler Titration Method Using YSI Dissolved Oxygen Meter Models 54, 57, and 58

8.6.1 The Winkler titration method (also referred to as the iodometric test) is the most precise and reliable titrimetric procedure for D.O. analysis (19^{th} Edition of Standard Methods for the Examination of Water and Wastewater). This method is excellent for calibrating the D.O. meter in the laboratory environment. Refer to Appendix B of this SOP for the preparation of the Winkler titration.

8.6.2 A Winkler Titration value is an averaged value obtained by determining the D.O. concentration on three samples containing dilution water (refer to Appendix B).

8.6.3 Prepare the meter as described in section 7.1 (Models 54 and 57) and 7.2 (Model 58).

8.6.4 As instructed in Appendix B, place the D.O. probe in the remaining BOD bottle filled with dilution water and gently stir. Wait for the reading to stabilize, then turn the selection knob to the appropriate mg/L range, using the 0_2 CALIB or CAL knob, and adjust until the meter reads the Winkler titration value. Again, when using the analog meter, select the appropriate mg/L range (0 to 5, 0 to 10 or 0 to 20 mg/L). Select the scale with the lowest range in which the value is contained.

8.6.5 The meter is now calibrated and ready to collect measurements.

8.7 Calibration by the Winkler Titration Method Using the YSI Handheld Dissolved Oxygen Meter Model 550

8.7.1 Switch the meter to milligrams per liter (mg/L) by pressing the MODE key.

8.7.2 To enter the calibration menu, press both the UP ARROW and DOWN ARROW keys at the same time. CAL will be displayed in the lower left of the display.

8.7.3 As instructed in Appendix B, place the D.O. probe in the remaining BOD bottle filled with dilution water and gently stir. Wait for the reading to stabilize, then using the UP and DOWN ARROW keys, enter the mg/L value obtained from the Winkler titration value, and press the ENTER key.

8.7.4 The meter will prompt you to enter the approximate salinity of the water that you are about to analyze. For freshwater systems, a value of zero parts per thousand (PPT) should be scrolled in using the UP or DOWN ARROW key.

8.7.5 Once the appropriate salinity value has been selected, press the ENTER key. The meter will then automatically advance to measurement mode. The meter is calibrated and ready to collect measurements in mg/L.

9.0 DISSOLVED OXYGEN MEASUREMENT

9.1 When determining D.O. measurements, place the D.O. probe directly into the water body for which a determination is to be made. The probe must either face into the current, move gently up and down in the water column (without breaking the surface of the water), or be used to gently stir the solution until the reading stabilizes.

9.2 Wait several seconds for the reading to stabilize and record the D.O. reading on the chain-of-custody record (refer to MDNR-FSS-002 *Field Sheet and Chain-of-Custody Record*) and/or in a field notebook. When using the analog meter, select the appropriate mg/L range (0 to 5, 0 to 10 or 0 to 20 mg/L). Select the scale with the lowest range in which the value is contained.

9.3 Between readings, the meter must be left on (any position other than off) and the D.O. probe stored within the calibration cap or a moist towel. If a significant amount of time (several hours) will pass between readings, the meter should be turned off to conserve battery life. Once the meter has been turned off, recalibration is required prior to collecting additional D.O. measurements.

10.0 METER AND PROBE STORAGE

10.1 The D.O. meters and probes are sophisticated electronic equipment that require care during their handling and operation. The meters and probes should be protected from jostling and/or sudden impacts during transportation, and sudden or extreme temperature changes.

10.2 At ESP the D.O. meters may need to be taken into the field at any time and they need to be available to field personnel at all times. For both short and long-term storage the probes should be stored ready for use in a container filled with deionized water or potassium chloride solution. This is important, both to keep the membranes moist and to prevent bubbles forming under the membranes resulting from the presence of a slight negative pressure in the ESP building. The manufacturer recommends the following methods of storage:

a. For long-term storage (longer than one month), the manufacturer recommends removing the membrane and draining the electrolyte (potassium chloride) solution from the probe. The probe should be rinsed and refilled with distilled water and a new membrane installed before storage. The probe should be stored in a humid environment such as the calibration chamber with a moist sponge inside or a container of distilled water.

b. For short-term storage (up to one week), the probes can be kept within the calibration cup with a moist sponge inside.

11.0 QUALITY CONTROL

11.1 If the meter is being used for long periods throughout a day, the meter should be periodically checked to make sure it is holding calibration.

11.1.1 For the YSI D.O. Models 54, 57 and 58: place the probe into the calibration bottle, switch the selection knob to TEMP, wait for the temperature to stabilize and read the air temperature. Refer to the solubility of oxygen chart located on the back panel of the meter (referred to on the meter as Table I). Read the correct calibration value in mg/L by referencing the air temperature reading with solubility of oxygen chart and correcting that calibration value to 700 ft altitude. Switch the selection knob to mg/L and read the D.O. If the meter is not capable of holding within ±1.0 mg/L of the stated calibration value (determined above), then the meter should be recalibrated.

11.1.2 For the YSI D.O. Models 550: place the probe into the calibration chamber, wait for the temperature to stabilize and read the air temperature. Refer to a solubility of oxygen chart and read the correction value in mg/L by referencing the air temperature reading with solubility of oxygen chart and correcting that calibration value to 700 ft altitude. If the meter is not capable of holding within ±1.0 mg/L of the stated calibration value (determined above), then the meter should be recalibrated.

11.2 A separate pocket thermometer that has been checked against a certified thermometer should be used to verify the accuracy of the D.O. meter's temperature readings during the air calibration procedure and periodically when collecting field measurements. The temperature readings should be within ± 1.0 degree °C of one another.

11.3 The ESP D.O. meters are subjected to monthly QC checks by WQMS personnel (refer to MDNR-WQMS-213 *Quality Control Procedures for Checking Water Quality Field Meters)*. The meters are air calibrated and checked against the Winkler titration method.

11.4 As part of quality control, all meters must be checked out by field personnel prior to field use. The following information shall be recorded on the equipment sign-out sheet: meter type(s) and property number(s), date meter(s) were checked out and returned, and the user's name. Upon return from the field, field personnel shall record any problems/comments when using the meter in the comment section of the sign-out sheet.

12.0 REFERENCES

MDNR-FSS-001 Required/Recommended Containers, Volumes, Preservatives, Holding Times and Special Sampling Considerations.

MDNR-FSS-002 Field Sheet and Chain-of-Custody Record.

MDNR-FSS-005 General Sampling Considerations Including the Collection of Grab, Composite, and Modified Composite Samples from Streams and Wastewater Flows.

MDNR-WQMS-213 Quality Control Procedures for Checking Water Quality Field Meters.

Standard Methods for the Examination of Water and Wastewater, 1995, 19th Edition, Section 4500-O B.

Code of State Regulations, Title 10, Department of Natural Resources, Division 20 – Clean Water Commission, Chapter 7, Water Quality

YSI Model 54ARC and 54ABP Dissolved Oxygen Meter Operations Manual.

YSI Model 57 Dissolved Oxygen Meter Operation Manual

YSI Model 58 Dissolved Oxygen Meter Operations Manual.

YSI Model 550 Handheld Dissolved Oxygen and Temperature System Operations Manual.

APPENDIX A
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TABLE I. SOLUBILITY OF OXYGEN IN WATER EXPOSED TO WATER SATURATED AIR AT 760 mm Hg PRESSURE

Temp °C	Solubility mg/L	Temp °C	Solubility mg/L	Temp °C	Solubility mg/L
0	14.62	16	9.87	32	7.31
1	14.22	17	9.67	33	7.18
2	13.83	18	9.47	34	7.07
3	13.46	19	9.28	35	6.95
4	13.11	20	9.09	36	6.84
5	12.77	21	8.92	37	6.73
6	12.45	22	8.74	38	6.62
7	12.14	23	8.58	39	6.52
8	11.84	24	8.42	40	6.41
9	11.56	25	8.26	41	6.31
10	11.29	26	8.11	42	6.21
11	11.03	27	7.97	43	6.12
12	10.78	28	7.83	44	6.02
13	10.54	29	7.69	45	5.93
14	10.31	30	7.56	46	5.84
15	10.08	31	7.43	47	5.74

TABLE II (in part). CALIBRATION VALUES FOR VARIOUS ATMOSPHERIC PRESSURES AND ALTITUDES.

Pressure inches Hg	mm Hg	kPa	Altitude Ft.	m	Calibration value (%)
30.23	768	102.3	-276	-84	101
29.92	760	101.3	0	0	100
29.61	752	100.3	278	85	99
29.33	745	99.3	558	170	98
29.02	737	98.3	841	256	97
28.74	730	97.3	1126	343	96
28.43	722	96.3	1413	431	95
28.11	714	95.2	1703	519	94
27.83	707	94.2	1995	608	93
27.52	699	93.2	2290	698	92
27.24	692	92.2	2587	789	91
26.93	684	91.2	2887	880	90
26.61	676	90.2	3190	972	89
26.34	669	89.2	3496	1066	88
26.02	661	88.2	3804	1160	87
25.75	654	87.1	4115	1254	86
25.43	646	86.1	4430	1350	85

APPENDIX B
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Calibration by the Winkler Titration Method

Equipment required:	**Reagents required:**
• 4-300 mL BOD bottles, glass stoppered • 25 mL titration buret with support stand • 250 mL graduated cylinder • eye-dropper • white background sheet	• manganese sulfate solution • alkaline iodide-azide solution • sulfuric acid • starch indicator solution • deionized water (dilution water) • sodium thiosulfate solution

Procedure:

1. With the D.O. instrument OFF, check the mechanical zero, if applicable.
2. Fill the four BOD bottles with dilution water.
3. Place the probe in one of the bottles. If applicable, turn the meter selection knob to RED LINE. Allow the meter to warm up 20-30 minutes for the probe to polarize.
4. To the remaining three bottles of dilution water:
   a) Add two droppers of manganese sulfate solution below the water line.
   b) Shake the alkaline iodide-azide solution and add two droppers above the water line.
   c) Stopper the bottles and invert bottle 15 times **(Do not allow air bubbles to be trapped in the bottles).** A brown flocculent indicates the presence of D.O.
   d) Let the floc settle half way down the bottle.
   e) Invert the bottles another 15 times.
   f) Let the floc settle a third of the way down the bottle.
   g) Add two droppers of concentrated H_2SO_4.
   h) Stopper the bottles and invert 5 times **(Do not allow air bubbles to be trapped in the bottles)**.
   i) Pour off 97-98 mLs (to make room for the titrant).
   j) Rinse the buret with sodium thiosulfate solution twice, then fill and zero.
   k) Add titrant to the BOD bottles until a pale straw-yellow color develops (approximately 7 mLs); without shaking the starch solution, draw one dropper full from the clear layer, add to each bottle and swirl without aerating the sample.
   l) Add titrant one drop at a time until the sample just turns clear (a white background behind the bottle will help determine when endpoint is reached).
   m) Average the values for the three bottles. This is the mg/L value of dissolved oxygen for the dilution water.